COPLANAR POLYCHLORINATED BIPHENYL (PCB) BACKGROUND CONTAMINATION IN TRACE LEVEL ANALYTICAL PROCEDURES

Joseph Ferrario, Christian Byrne, Aubry E. Dupuy, Jr.

U. S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances, OPP/BEAD/ACB
Environmental Chemistry Section, John C. Stennis Space Center, Mississippi 39529

INTRODUCTION

The relatively recent addition of the "dioxin-like" PCB congeners to the assessment of risk associated with the 2,3,7,8-chlorine substituted dioxins and furans has dramatically increased the number of laboratories worldwide that are developing analytical procedures for their detection and quantification. Most of these procedures are based on established sample preparation and analytical techniques employing High Resolution Gas Chromatography High Resolution Mass Spectroscopy (HRGC/HRMS) used for the analyses of dioxin/furans at low parts-per-trillion (ppt) levels. A significant and widespread problem that arises when using these sample preparation procedures for the analysis of coplanar PCBs is that the method blanks contain various levels of these PCB congeners. This contamination is due to the global distribution of these compounds via the atmosphere resulting in ubiquitous air contamination.[1)] Reliable procedures were developed to accurately define these background levels and assess their variability over the course of the study. The background subtraction procedures developed and employed ensure that the values reported accurately represent the levels found in the samples and were not biased due to contamination.

INTRODUCTION

The U.S. EPA Dioxin Reassessment Program has recently required that the dioxin-like PCB congeners be added to the list of 2,3,7,8-chlorine substituted dioxins and furans when considering the total toxic equivalent (TEQ) resulting from the various congeners.

As part of the U. S. EPA's Program to measure these dioxin-like congeners in various food items, beef fat samples originally collected as part of a statistically designed national survey to determine the levels of dioxins and furans were re-analyzed for the following dioxin-like coplanar PCBs: 77, 126, 169, 105, 118, 156 and 157.

During the method development phase of the study, we were confounded at finding the congeners in our method blanks at concentrations that prevented the analysis of samples at the desired low ppt levels. The relative distribution of these congeners in our method blanks reflected that found in the various PCB commercial mixtures[2)] and is consistent with the amounts and relative distribution found by other investigators.[1,3)]

After repeated efforts at modifying the analytical procedure failed to sufficiently reduce the background, we moved the sample preparation activities into a mobile lab trailer isolated from the main building. The trailer was equipped with a five ton air conditioner and the air was filtered through several layers of activated charcoal. The air flow was sustained at a level that resulted in the trailer maintaining positive pressure, thereby substantially reducing any inflow of unfiltered air.

These efforts resulted not only in a reduction in the actual concentration of these congeners but also a decrease in the variability associated with the various PCB congeners in our method blanks The results are shown in Table 1.

Table 1. **Concentrations of PCBs (pg/μl) in Method Blanks Before and After the Introduction of an Air Filtration System.**

PCB Congener	PCB 77	PCB 118	PCB 105	PCB 126	PCB 156	PCB 157	PCB 169
BEFORE (N-14)							
Average	3.7	79	54	0.33	26	5.6	N/D*
StdDev	1.8	53	37	0.18	28	6.0	-
%RSD	50	68	68	53	106	107	-
AFTER (N=18)							
Average	1.4	35	15	0.07	4.0	0.8	N/D*
StdDev	0.4	14	6.0	0.02	2	0.4	-
%RSD	31	41	41	27	49	51	-

* Not detected in method blanks

ANALYTICAL METHODS

During the course of this ten-week study period to determine the concentration of the PCB congeners in beef fat samples, sixteen method blanks were generated. Sample sets consisted of 12 possible sample positions including one or two method blanks, one control matrix, one laboratory control matrix fortified with the native congeners, and eight or nine field samples.

The analytical and QA/QC methods employed were similar to those described in U. S. EPA Method 1613[4] with modifications[5].

Briefly, a 10g sub-sample taken from a 100g homegenate of beef fat was fortified at

10 ppt with ^{13}C labeled surrogates and extracted with methylene chloride using a tissue homogenizer. The lipid was removed by stirring the crude extract with acid-impregnated silica gel and passing the extract through an acid/base silica gel column.

The coplanar PCBs were separated from the other non-target PCBs and from the dioxins and furans using graphitized carbon columns consisting of a 95/5 mixture of Biosil A (100/200 mesh) and AMOCO PX-21 carbon. The separations were achieved using the following elution procedure: 5 ml of 25/75 methylene chloride/hexane (this fraction contains the non-planar PCBs and was discarded); 5 ml methylene chloride (this fraction contains the mono and di-ortho PCBs 105, 118, 156, and 157); 14 ml 75/25 benzene/methylene chloride (this fraction contains non-ortho PCBs 77, 126 and 169). The column can now be reversed and the dioxin/furans eluted with 14 ml of toluene.

The two fractions containing the coplanar PCBs were combined and reduced in volume, fortified with ^{13}C internal standards and further reduced to a 20 µl final volume. One µl was analyzed using a 60 meter DBS-MS column by HRGC/HRMS. The KRATOS Concept® mass spectrometer was operated in the mass drift correction mode and the native analyte concentrations were determined by isotope dilution.

RESULTS AND DISCUSSION

Background contamination is an important consideration when analyzing samples for compounds at the ppt level that are also ubiquitously distributed in the environment. In fact, background contamination will define the lower limit of detection if it cannot be eliminated. In cases where background contamination is routinely present, the central issue to be resolved is the level of background that can be reliably determined to be "real" (i.e., contributed from the sample matrix). To define the level of background contamination and its variability over the course of a study, one must retrospectively examine the method blanks.

Table 2. **Concentrations of the PCBs (pg/µl) in Method Blanks (N=16)**

PCB Congener	Mean	StdDev	%RSD	Mean+1 sig.	Mean+2 sig.
77	1.39	0.44	31.4	1.83	2.26
118	33.7	13.8	40.9	47.5	61.3
105	15.6	6.49	41.6	22.1	28.6
126	0.07	0.02	30.7	0.09	0.11
156	3.86	1.91	49.5	5.77	7.68
157	0.78	0.41	51.6	1.18	1.59
169	-	-	-	-	-

The results from the analysis of the method blanks are shown in Table 2 along with the mean and standard deviation for each congener. Also included in the table is the mean + 1 standard deviation (sigma) and the mean + 2 sigma for each congener. The values shown for PCB 126, in most cases, represents chemical interference at the retention time of PCB 126. Isotope and S/N ratios were insufficient for a positive identification but a value was generated since it would contribute to the total amount of PCB 126 when analyzing samples.

After examining the blanks, we decided to subtract from each sample the mean value plus 2σ for each congener. The resulting value was greater than 95% (17/18) of the method blanks for each congener and, in most cases, was greater than all the method blanks.

No value for an analyte was reported until the amount remaining after background subtraction exceeded 1 standard deviation unit of the mean of the blank values for that particular congener.

This method of background determination and subtraction is quite conservative and increases the possibility of false negatives for values close to the detection limits. It also tends to increase the method's limits of detection and quantitation (LOD/LOQ). However, it also increases the confidence associated with values near the LOD and minimizes the likelihood of false positives.

These procedures resulted in the following LOD/LOQ above background (values are lipid adjusted in ppt): PCB 77, 1.0/1.0; PCB 118, 30/30; PCB 105, 15/15; PCB 126, 0.4/0.4; PCB 156, 14/14; PCB 157, 1.0/1.0; PCB 169, 0.2/0.3

The procedures used to determine the amounts and variability of background contamination are of increasing importance as detection limits continue to be reduced.

References

[1] Alcock, R.E., C. J. Halsall, C.A. Harris, A. E. Johnston, W. A. Lead, G. Sanders, and K.C. Jones (1994) Contamination of Environmental Samples Prepared for PCB Analysis. Envir. Sci. & Technol. 28: 1838-1841.

[2] Schulz, D.E., G. Petrick, and J. C. Duinker (1985) Complete Characterization of Polychlorinated Biphenyl Congeners in Commercial Aroclor and Clophen Mixtures by Multidimensional Gas Chromatograph-Electron Capture Detection. Envir. Sci. Technol. 23: 852-859.

[3] deBoer, J., C.J.N. Stronck, F van der Vaik, P.G. Wester, and M.J.M. Davdt (1992) Method for the Analysis of Non-Ortho Substituted Chlorobiphenyls in Fish and Marine Mammals. Chemosphere 25, 7-10: 1277-1283.

[4] USEPA Office of Water Engineering and Analysis Division (1994) Method 1613: Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, U.S. Government Printing Office: Washington, DC, Revision B.

[5] Ferrario, J.F., C. Byrne, D. McDaniel, A. Dupuy, and R. Harless (1996) Determination of 2,3,7,8-Chlorine-Substituted Dibenzo-p-dioxins and -furans at the Part per Trillion Level in United States Beef Fat Using HRGC/HRMS. Analytical Chemistry 68-4: 647-652.

Acknowledgement

We thank the following people for their assistance in various stages of this study: Stanley Mecomber, James Gibson, and Ray Shaw, EPA/ECS, for their extraction and cleanup of the samples; Danny McDaniel, EPA/ECS, for his suggestions and guidance, Matthew Lorber and David Cleverly, EPA/ORD, for the overall coordination of the dioxin program, and Geraldine Pierce for her expert assistance in the preparation of this manuscript.